

TA012 Dielectric Property Measurements and Techniques
**STUDIES ON THE DIELECTRIC BEHAVIOUR OF POLYPYRROLE AND ITS SEMI
INTERPENETRATING NETWORKS WITH POLY (VINYL CHLORIDE) IN THE MICROWAVE
FIELD**

*Honey John¹, Rinku M.Thomas¹- Rani Joseph¹ * K.T. Mathew²*

*1-Department of Polymer Science & Rubber Technology, 2-Department of Electronics
Cochin University of Science and Technology, Kochi- 682 022, INDIA, Tel: +91 484 2576418,
Fax: +91 484 2575800
E-mail: ktm@cusat.ac.in, URL: <http://www.doe.cusat.edu>*

ABSTRACT

Polypyrrole/poly (vinyl chloride) semi interpenetrating networks are found to exhibit dielectric properties higher than that of Polypyrrole alone in the microwave frequencies. Polypyrrole was prepared using ammonium per sulfate initiator at room temperature, and the dielectric properties in the microwave frequencies were measured. Polypyrrole/poly (vinyl chloride) semi interpenetrating networks of different compositions were prepared in pellet form and film form and their dielectric properties were studied at different microwave frequencies. An HP 8510 Vector network analyzer interfaced with a computer was used. Cavity perturbation technique was employed for the study. The dielectric properties like permittivity, dielectric loss, dielectric conductivity, dielectric heating coefficient, loss tangent, and absorption coefficient and penetration depth were studied. Key words: Polypyrrole, Poly (vinyl chloride), Cavity perturbation technique, dielectric properties.

INTRODUCTION

In recent years conducting polymers with conjugated double bonds have attracted much attention as advanced materials. Polypyrrole (PPy) is especially promising for commercial applications because of its good environmental stability, facile synthesis, and higher conductivity than many other conducting polymers. Incorporation of conducting polymer into a host polymer substrate forming a blend, composite or inter penetrated bulk network has been widely used as an approach to combine electrical conductivity with desirable physical properties of polymers^{1,2}. Polypyrrole is considered as one of the most promising candidate for the fabrication of conductive blends / composites/inter penetrating networks (IPN's) with industrially important class of polymers³.

EXPERIMENTAL

Preparation

1. Polypyrrole

Chemical oxidative polymerization of pyrrole is carried out using ammonium per sulphate as initiator⁴ in the presence of 1M HCl. The polymerization is carried out for 4 hrs. At room temperature. It is then filtered, washed and dried under different conditions like room

temperature (48 hrs.), in oven (at 50-60°C for 6 hrs.), in vacuum (at room temperature, for 16 hrs.). The dielectric properties of the all samples are studied using cavity perturbation technique.

Preparation of PPy/PVC SIPN

Chemical oxidative polymerization of pyrrole / polyvinyl chloride SIPN is also prepared by the insitu polymerization of pyrrole using the above procedure in the presence of polyvinyl chloride powder. Different proportions as 1:1,1:1.5,1:2,1:2.5 are prepared, the samples are pelletised and the dielectric properties are measured at S band (2-4 GHz). Polypyrrole / Polyvinyl chloride (PPY/PVC) SIPN in soluble form is prepared by using emulsion grade polyvinyl chloride solution in Cyclohexanone. It is then made in to film by solution casting and is doped with 1M HCl. Different compositions of PAN-PVC SIPN's, (2:1,1:1,1:2,1:3) is prepared. It is very difficult to prepare the film of SIPN's of 2:1and 1:1 PPy: PVC compositions.

EXPERIMENTAL SET UP AND THEORY

The experimental set up⁵ consists of a HP8510 vector network analyzer; sweep oscillator, S- parameter test set and rectangular cavity resonator. The measurements were done at 25⁰ C in S band (2 GHz - 4 GHz). When a dielectric material is introduced in a cavity resonator at the position of maximum electric field, the contribution of magnetic field for perturbation is minimum. The field perturbation is given by Kupfer et al⁶.

The real and imaginary parts of the relative complex permittivity are given by

$$\epsilon_r' = 1 + \frac{f_o - f_s}{2f_s} \left(\frac{V_c}{V_s} \right), \quad \epsilon_r'' = \frac{V_c}{4V_s} \left(\frac{Q_o - Q_s}{Q_o Q_s} \right)$$

The real part of the complex permittivity, ϵ_r' is generally known as dielectric constant and the imaginary part ϵ_r'' of the complex permittivity is related to the dielectric loss of the material.

The loss tangent is given by, $\tan \delta = \text{loss current}/\text{charging current} = \epsilon'' / \epsilon'$, where ϵ' is the measured dielectric constant of the dielectric material and ϵ'' is the loss factor or loss index.

Here $\sigma + \omega\epsilon_r''$ is the effective conductivity of the medium. When the conductivity σ due to free charge is negligibly small (good dielectric) the effective conductivity is due to electric polarization and is reduced to $\sigma_e = \omega\epsilon_r'' = 2 \pi f \epsilon_0 \epsilon_r''$

The efficiency of heating is usually compared⁵ by means of a comparison coefficient J, which is defined as $J = 1/\epsilon_r \tan \delta^7$. The absorption of electromagnetic waves when it passes through the medium is given by the absorption coefficient⁷ (α_f), which is defined as, Absorption coefficient (α_f) = $\epsilon_r'' f / n c$, Where $n = \sqrt{\epsilon^*}$ and 'c' is the velocity of light.

Penetration depth, also called as skin depth, is basically the effective distance of penetration of an electromagnetic wave into the material⁷, Skin depth (δ_f) = $1 / \alpha_f$

RESULTS AND DISCUSSION

Variation of dielectric properties with compositions

Dielectric loss and conductivity

Figure 1a & 1b shows the dielectric loss and conductivity of different compositions of PPy: PVC SIPN in pellet and film form respectively at 2.97 GHz.

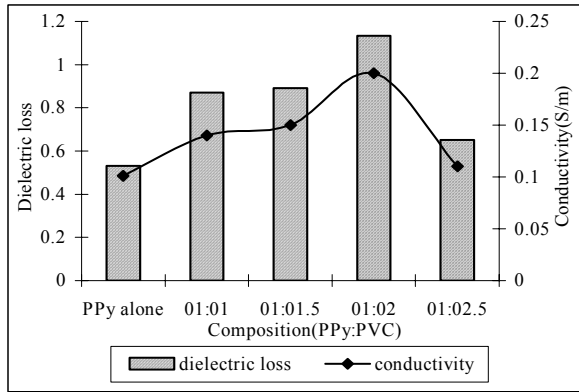


Figure 1a

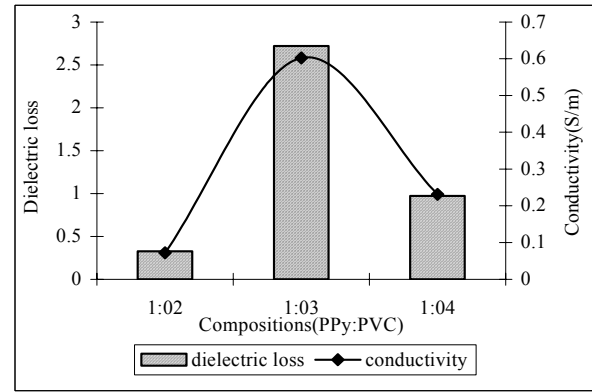


Figure 1b

It is clear from the figure that the dielectric loss and conductivity increases with increase in PVC content and it reaches a maximum at 1:2 proportion in pellet form and 1:3 in film form, due to the interfacial polarization of matrix⁸ with two dielectric constants.

Dielectric heating coefficient (J)

It is clear from the figures 2a and 2b that the dielectric heating coefficient is minimum for 1:2 compositions in the case of pellet form and 1:3 in the case of film form.

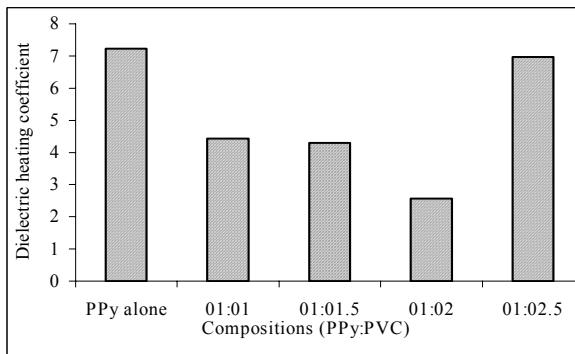


Figure 2a

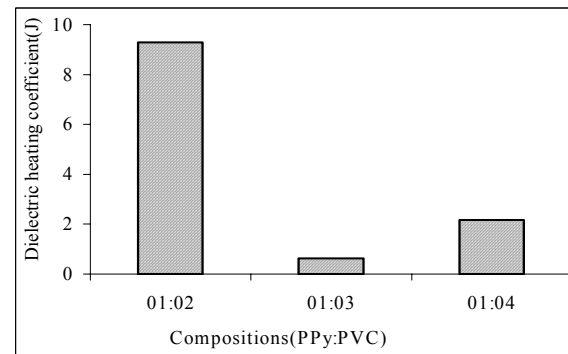


Figure 2b

These compositions are suitable for dielectric heating applications.

Absorption coefficient and skin depth.

Figure 3 and table 1 shows the variation of absorption coefficient and the skin depth of different compositions of SIPN's in pellet and film forms respectively at 2.97 GHz. Since the absorption coefficient is directly related to the dielectric loss factor the absorption coefficient is

higher for 1:2 composition in pellet form and 1:3 in the case of film form. The skin depth is least for these compositions.

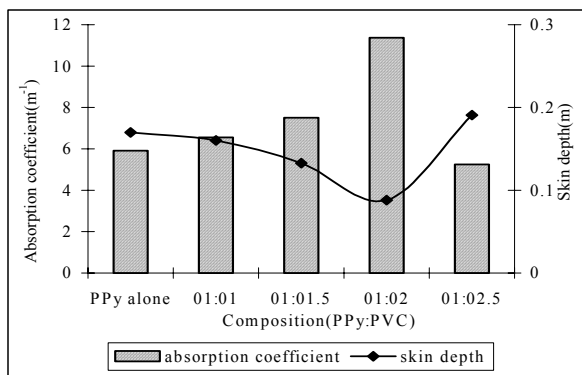


Figure 3

Table 1

	Composition (PPy: PVC)		
	1:2	1:3	1:4
Absorption coefficient (m ⁻¹)	4.5	27.61	22
Skin depth (m)	.22	.04	.07

From all these properties the 1:2 Pani: PVC composition in the case of pellet form and 1:3 composition in the case of film is optimized.

Variation of dielectric properties with frequency: Figure 4 shows that the variation of the imaginary part of the complex permittivity or the dielectric loss factor ϵ'' , of different proportions of SIPN's with frequency. The dielectric loss is found to increase with frequency with a slight dip in the middle frequencies.

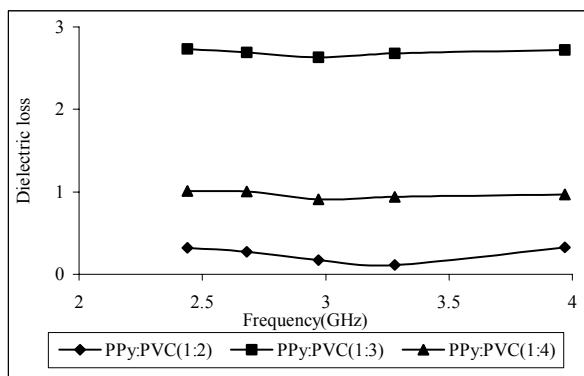


Figure 4

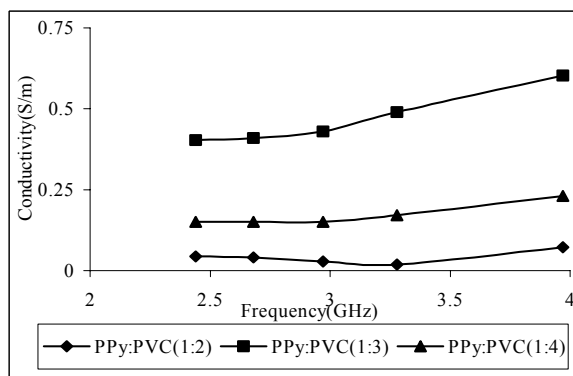


Figure 5

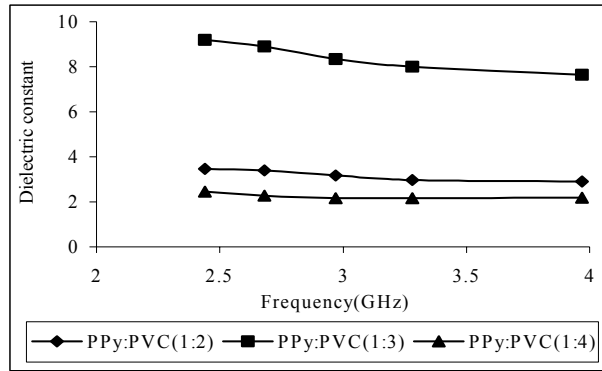


Figure 6

This is in agreement with the pellet form of SIPN. **Figure 5** indicates that the conductivity also shows the same behavior as dielectric loss. The real part of complex permittivity i.e. the dielectric constant of the SIPN's decreases with increase in frequency as shown in **figure 6**. At higher frequency, the orientation polarization-takes place and this lead to a high dielectric loss and this results in decrease of dielectric constant.

Figure 7 shows the variation of dielectric heating coefficient for different proportions with frequency. The $\tan\delta$ is directly related to the dielectric loss factor and it also shows the same behavior as that of dielectric loss.

Figure 8 shows the variation of loss tangent of different SIPN's with frequency. It is observed that the heating property increases with increase in frequency. It is clear from the figure that the dielectric heating coefficient is less at higher frequency.

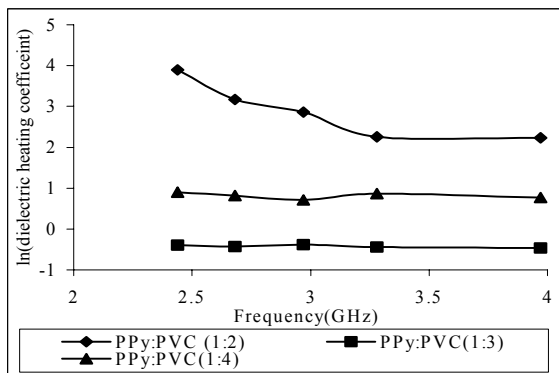


Figure 7

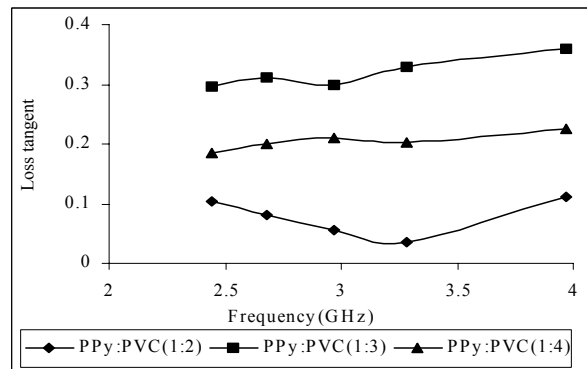


Figure 8

Comparison of pellet and film form of PPy: PVC SIPN

Table 2 shows the dielectric properties of SIPN's of pellet (1:2 PPy: PVC composition) and film (1:3 which shows better results than 1:2 film) forms. It is clear from the table that the conductivity and absorption coefficient are higher for film sample and the dielectric heating

coefficient and skin depth are lower for the film samples, due to the better dilution effect of film samples.

Table: 2:

	1:2 (PPy: PVC)	1:3(PPy: PVC)
Conductivity (S/m)	0.2	0.602
Dielectric heating coefficient	2.56	0.63
Absorption coefficient (m ⁻¹)	11.36	38.97
Skin depth (m)	0.09	0.03

CONCLUSIONS

The film form of SIPN is superior to pellet form in terms of conductivity, heating coefficient, and absorption coefficient and skin depth. The dielectric loss and conductivity are higher for 1:2 PPy: PVC composition in pellet form and 1:3 composition in film form. The dielectric heating coefficient is minimum for 1:2 compositions for pellet samples and 1:3 compositions for film samples. The absorption coefficient of 1:2 compositions for pellet samples and 1:3 compositions for film samples are high. The skin depth of 1:2 compositions for pellet samples and 1:3 compositions for film samples are less.

REFERENCES

1. B.Tieke and W. Gabriel, *Polymer*, **31**,20,(1990)
2. T.Kunugi,H.Okazaki, *Jpn.Kokai Tokyo Koho JP11 159,443*,(99,159,443).
3. H. S. O. Chan, H. Hopok, E. Khor.and M. M. Tan., *Synth.Met.*, **31**, 95, (1995)
4. Y.Liu, G.Shi, C.Li.Y.Liang, *J.Appl.Poly.Sci.*, **70**,2169,(1998).
5. K.T.Mathew and U.Raveendranath, Waveguide cavity Perturbation method for measuring complex permittivity of water, *Microwave and Optical Technology Letters*, (USA). **Vol.6**, No.2, pp. 104-106,(1993).
6. Klaus Kupfer, A Kraszewski and r Knoochel, *Sensors update Vol.7*. Cavity perturbation techniques for measuring dielectric parameters of water and other allied liquids.Wiley-VCH, Germany,186-209, (2000).
7. Chen. C. Ku; Raimond Liepins, *Electrical Properties of Polymers: Chemical Principles*, Hanser Publishers: (1987).
8. J.C.Maxwell, *Electricity and Magnetism*, Oxford University Press, Oxford (1892).